Reagecon

"Delivering The Correct Result..."

Turbidity Standards and Reference Materials

A REAGECON TECHNICAL PAPER

Authors: John J. Barron
www.reagecon.com

Turbidity Standards and Reference Materials

Author: John J. Barron – Managing Director, Reagecon Diagnostics Ltd, Shannon Free Zone, County Clare, Ireland

Abstract

High quality turbidity standards and controls are required for precise and accurate on-line, field and laboratory turbidity measurements. This paper introduces a new range of such standards that are formazin-free and provides the first detailed description of how their features and characteristics facilitate all aspects of good laboratory practice (GLP). The new standards are compared and contrasted with the formazin standards from a GLP, Health & Safety, stability and cost saving perspective and are shown to offer unequivocal advantages under all of these categories. The paper concludes that such standards should always be used in preference to formazin based standards.

1 Introduction

Turbidity is a test of drinking water, both raw and treated, which is very regularly performed but sometimes poorly understood. Not only is turbidity a key indicator of water quality but it can also be used as a key determinant of chemicals used to reduce suspended solids in water. In many other types of liquids and solutions, turbidity can be caused by particulate matter detrimental to the end use or by particles that are vital to the product or process. A comprehensive list of the applications of turbidity monitoring and control are outlined in Table 1.

The purpose of this paper is to define turbidity, briefly discuss some of the instrumentation currently used to measure turbidity and discuss in detail the current state of the art as regards Standards and Reference Materials for turbidity measurement.

2 Definition of Turbidity

Turbidity comes from the Greek word 'turbid' which in simple terms means cloudy, hazy, or not pure. All drinking water, both raw and treated contains some degree of turbidity due to dispersed suspended solids such as silt, clay, algae, organic/inorganic matter or micro organisms. Although there are a number of methodologies available to measure the amount of suspended solids by far the most practical and commonly used technique is turbidity measurement.

Simply put, turbidity is an optical property of the interaction between light and suspended solids in water. When a beam of light is passed through ultra-pure water its path remains relatively undisturbed. However, particulate suspended solids will interfere with the light beam and absorb the light energy and/or scatter or reflect the light.

Water/Waste Water	General Quality, Microbial contamination, Quality Fluctuations, Trends, Sedimentation, Coagulation, Flocculation processes, Filtration, Efficiency, Suspended Solids, Regulatory Compliance
Biotechnology Research	Continuous Cell Culture, Bacterial Growth, Chemostat Management
Food/Beverage Industry	Aesthetics, Process Membrane Filtration Efficiency, Microbiology, Microbial Contamination, Clarity, Dissolution
Electroplating	Sulphate Measurement, Aesthetics of Finished Products, Effluent Monitoring
Pure Waters/Steam	Silica Monitoring
Pulp & Paper	Iron Particulates
Geothermal Power Plant	Indirect measurement of particulate iron

Table 1: Applications of Turbidity Monitoring and Control

3 Turbidity Measurement

Accurate and precise laboratory or on-line analytical measurement can be influenced by the following 5 key parameters:

- Measuring Instrument
- Measuring Accessories
- The Sample
- The Operator
- Standards and Reference Material

The technical validation, comparability, quality control/assurance, proficiency testing and traceability of any analysis require significant attention to detail of all these parameters. Turbidity measurement is no different in this respect. Although the primary focus of this paper is on the Standards/Reference Materials, it is worth discussing by way of background in brief detail all of the other parameters.

3.1 Measuring Instrument (Turbidity Meter)

Since most turbidimetric measurement is carried out on a nephelometric turbidity meter it is worth analysing the major components of this type of instrument. The United States Environmental Protection Agency (USEPA), the American Society for Testing Materials (ASTM) and Standard Methods have strict criteria for these components which are as follows:

- Light source is a tungsten lamp operated at a colour temperature of between 2200K and 3000K.
- Distance traversed by the incident light within the sample not to exceed 10cm.
- Detector shall be centred at 90° to the incident light not to exceed ±30° from 90°.
- The detector and filter system if used should have spectral properties that include clear colourless glass, free from scratches and fingerprints.
- The sensitivity of the instrument should permit detection of a turbidity difference of 0.02 units or less in water that has turbidity of 1NTU or less.

These nephelometric instruments are also termed non-ratio instruments, the layout of which is outlined in Figure 1.

The design criteria for the instrument are broad in their acceptance limits. This may account for large variances that are encountered from instrument to instrument and in practice it is common to get different readings for the same sample from instruments from different manufacturers. However, the function of good quality Standards and Reference Materials is to regularise these anomalies and ensure that the readings obtained from different instrumentation are as close to each other and as close as possible to the true value.

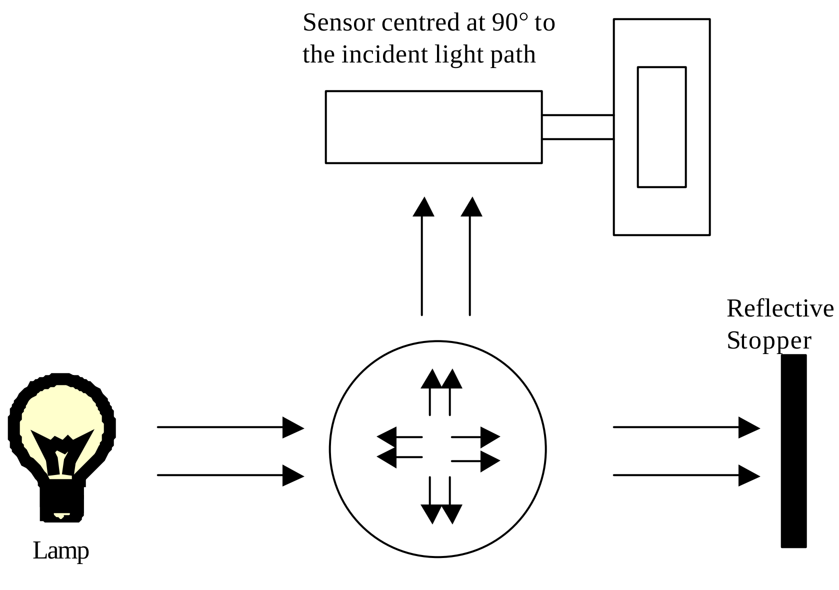

Figure 1: Simple Schematic of Turbidity Meter

Some modern instrumentation works on the basis of a modification of the standard nephelometric method for turbidity measurement. Such measurements not only detect light scattered at right angles from a detected beam. Such instruments may have multiple detectors at various angles, not necessarily including 90°, or a single detector positioned at an angle other than 90°. These designs compensate for colour, haze or suspended particles that are larger than one micron in size. Such instruments are called ratio turbidimeters.

3.2 The Cuvette

A critical component of turbidimetric measurement is the cuvette. Glass thickness may vary from cuvette to cuvette and even within the same cuvette. This can be a problem with light scatter measurement, particularly in the low NTU levels encountered in drinking water analysis. Correct use of the cuvette is vital and the user must ensure that it is clean; clear; free from scratches, smudges, fingerprints and, above all, that it is indexed.

Indexing is a simple procedure designed to eliminate variances in the glass from affecting your readings. It assures the same light passage through the cuvette for both Standard and Sample. Indexing of the cuvette entails finding the point of the cuvette that light passes through that gives the lowest reading. This point and the corresponding point on the cuvette holder should be marked indelibly and these marks should be aligned for all future readings.

3.3 The Sample

Sample handling, preparation, shipping and storage are crucially important factors in obtaining true values in any analytical measurement. If the test portion is not representative of the original material it will not be possible to relate the analytical result to the original material, no matter how good the analytical method used nor how carefully the analysis is performed.

The final result may be dependent on the analytical method, but it will always be dependent on the sampling process. All equipment used for sampling, sub-sampling, sample handling, sample preparation and sample extraction should be selected to avoid unintended changes to the nature of the sample that may influence a final result. The sampling of material for turbidity measurement must follow the same stringent criteria. With this sample the critical factors are the physical properties: particle size, distribution, shape and refracted index. It is important that no part of the sampling regime interferes with any of these parameters.

3.4 The Operator

To measure turbidity like any other analytical measurement consistently it is important to understand the technique, the working of the instrument, the necessity of proper sampling and the use of correct standards.

4 The Standard / Reference Material

The nephelometric turbidity meter is designed to be routinely standardised with a known light scattering standard. As with all analytical standards or reference materials, a turbidity standard should fulfil the following criteria:

- Provide traceability.
- Demonstrate the accuracy of results.
- Calibrate the equipment and methodology.
- Monitor the user performance.
- Validate the test.
- Facilitate comparability i.e. to ensure that when the correct procedures have been followed the same analysis of the same materials will produce results that agree with each other whenever they are performed.

Standards and Reference materials should be produced and characterised in a technically competent manner, should be homogenous, stable, certified and have available a known uncertainty of measurement. Presently, there are only two standards recognised and approved by the USEPA, Standard Methods, ASTM and other regulatory agencies, these are formazin and AMCO AEPA-1.

4.1 Formazin

Formazin is an aqueous suspension of an insoluble polymer formed by the condensation reaction between hydrazine sulphate and hexamethylenetetramine (see Figure 2). Although formazin was suggested as a turbidity standard as early as 1926 it has many limitations which can be summarised as follows:

- The working standards made from diluting 4000NTU stock standard are less stable than the original stock. In fact, even the stock solution may be only within a ±10% variation from batch to batch in many cases.

- Formazin begins to settle out immediately and agglomerate easily, making it difficult to hold a stable, reproducible or repeatable reading. This is particularly significant in the lower turbidity ranges such as 0 to 5NTU where formazin standard is very unpredictable.
- Working formazin standard of up to 400NTU only has a shelf life of 1 month if the user is to follow the recommended EPA and Standard Methods regulations. Lower concentration formazin standards are required to be prepared weekly or even daily. The reason for this is formazin is difficult to hold in suspension and begins to agglomerate almost immediately.
- The diluent for formazin standards must be turbidity free water. This is often difficult to obtain particularly in a field situation.
- Formazin is a very toxic chemical and one of the chemicals from which it is derived, hydrazine sulphate, is a known carcinogen. Even substantial dilutions of the 4000 NTU formazin standard have been shown to have significant parts per million (ppm) of hydrazine sulphate and even when diluted to very low concentrations can cause a health hazard.
- The carcinogenic nature of this toxic chemical and the inconvenience of constantly having it diluted to the values needed are both overshadowed by the inaccuracy of the results that sometimes occur when tests in turbidity meters, calibrated with formazin are performed in the 0 to 1 NTU range.
- The number of dilution steps necessary to get from a 4000 NTU stock standard to a lower range working standard is significant. Most plants or field sites are not equipped with the necessary volumetric glassware, pure water or controlled conditions to adequately perform these dilutions

Apart from the aforementioned logistics there are other compulsive reasons why formazin lacks suitability as a turbidity standard.

- Particle size and shape are irregular. Size may vary from 1.75 micron to 20 microns.
- The average particle size in drinking water is on order of magnitude smaller than that of formazin which inherently invalidates formazin as a meaningful standard.

4.2 AMCO AEPA-1 Standard

Fortunately, since 1982, there is a standard available which overcomes the shortcomings of formazin. This has been developed by the American Company, Advanced Polymer Systems, and is a suspended mixture of styrene divinylbenzene polymer spheres. These standards have the following characteristics:

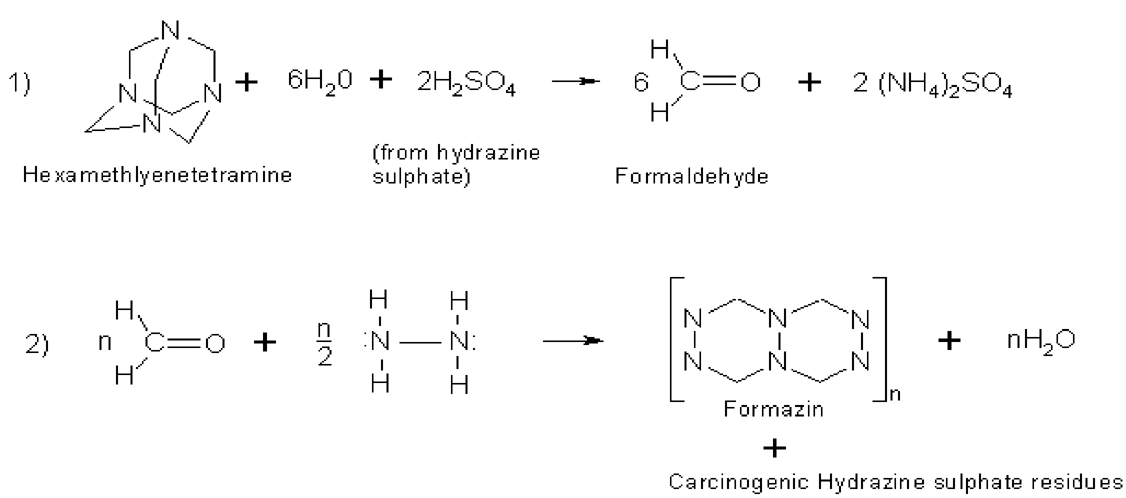

Figure 2: Preparation of Formazin

- Stability
  AMCO APEA-1 turbidity standards are a stabilised suspension of cross linked styrene divinylbenzene copolymer microbeads in ultrapure water. These beads are chemically inert and keep their chemical balance in a water medium regardless of concentration. The size scatter of the beads only ranges from 0.06 to 0.2 microns. This small size accounts for random Brownian movement of these beads in suspension, keeping them in constant motion and totally dispersed within the ultra pure water matrix.

- Physical properties
  Particle size, uniform shape and refractive index make these spheres ideal to characterise light absorption and scatter for 90° behaviour in the UV-Vis range. In addition the bead's spherical shape and size impedes the agglomeration or precipitation of the standard. For these reasons the AMCO AEPA-1 standards are very stable. They have guaranteed shelf life of 1 year (if kept free from contamination) and will only agglomerate or settle out if frozen accidentally. The main preventative measure necessary for long term use of these standards is to avoid bacterial contamination by using good laboratory handling techniques and storage.

- Reliability
  These standards are prepared and bottled in a clean room facility. They are tested for accuracy and stability, fully validated before bottling, and free from any toxic or carcinogenic chemicals or compounds.

- Flexibility
  These standards are available from 0 to 4000 NTU. All are ready to use, and there is no risk of error due to dilution or contamination or safety implications for the user. This means that each standard can be issued with a Certificate of Analysis which gives complete traceability back to the Primary Standard.

A summary of the differences between formazin and the AMCO APEA-1 turbidity standard is outlined in Table 2.

Feature	AMCO APEA -1	Formazin
Toxicity	Non-toxic. No special handling or disposal requirements	Very toxic, contains a known carcinogen. Requires special handling and disposal
Particle shape & size	Well defined spherical shape. Mean diameter is 0.06µm with a distribution between 0.01 and 0.2µm.	Irregular shape and distribution. Mean diameter is 3µm with a distribution between 1 and 20µm.
Shelf life	Does not deteriorate or settle out. A long stable shelf life at all concentrations.	Flocculates and deteriorates. Lower concentrations change value within days, or hours, after preparation.
Particle suspension	Particles stay in suspension. Mixing is discouraged as it entrains air.	Particles settle quickly, suspension must be continuously mixed. Mixing induces shearing.
Traceability	Certified traceable to NIST Reference Material 1690	Non traceable
Precision (batch to batch)	Mean of SD's 0±0.00	Mean of SD's 0.9±0.2
Inter-instrument reproducibility	0.5 ±0.0	0.8±0.2
Stability	0.1 – 4000 NTU (1 year)	4000 NTU (3 months). Need for dilutions to be prepared daily or weekly.
Accuracy	±1% (all values)	±10% (4000 NTUs) up to ±30% for dilute working standards.

Table 2: Comparison of AMCO EPA-1 and Formazin Turbidity Standards

5 Conclusion

Turbidity measurement is a quick and inexpensive test that can help operators diagnose and treat water problems. Proper calibration technique and the use of high quality turbidity standards, such as the AMCO AEPA-1 standards, ensure that measurements can be fully validated, are in compliance with regulatory requirements, are traceable to Primary Reference Materials and, most importantly, are comparable. The user can be certain that their measurements irrespective of instrument are all traceable in an unbroken chain to the same NIST Primary Standard. If an external proficiency testing scheme or inter-laboratory study is participated in the user can be confident that results will have a high degree of accuracy, precision and agreement. Of course, there is another benefit to using top quality AMCO APEA-1 standards and that is chemical savings. When chemical treatment is part of the programme the cost of non-effective or poor calibration will be significant and major losses may occur due to excessive quantities of chemical being added to water based on erroneous turbidity measurements.

5 Bibliography

1. Vanous, R.D, "Understanding Nephelometric Instrumentation". American Laboratory July 1978
2. Spair, J.A., "A Primer in Turbidity". Advanced Polymer Systems Inc., Redwood City, California 193
3. Hach, C.E., Vanous, R.D., Heer, J.M., "Understanding Turbidity Measurement". Technical Information Booklet, Series 11, 1982
4. Heer, J.M, "Turbidimetric Standards, Calibration & Practice". Waterworld News, Vol. 3, No. 3, 1987
5. Papacosta, K., "The Principle of Non-Ratio -v- Ratio Turbidimeter and the effects of various particle sizes tested". Advanced Polymer Systems Inc., Redwood City, California, 1990.
6. Papacosta, K., SPair, J.A., Katz, M., "The rationale for the establishment of a certified reference standard for nephelometric instruments". Advanced Polymer Systems Inc., Redwood City, California, 1990.
7. Papacosta, K., Almeda, A. "The turbidity measurement factors for accuracy". Advanced Polymer Systems Inc., Redwood City, California.
8. "Standard Methods for Turbidity of Water", American Society for Testing & Materials, ASTM Designation B1889294
9. "Manual for certification of laboratories analysing drinking water", United States Environmental Protection Agency EPA814892, September 1992.
10. O'Dell, J.W., "Determination of turbidity by nephelometry". Method 180.1 Environmental Monitoring Systems Laboratory Office of Research and Development, USEPA, Cincinnati, Ohio.
11. EPA 1978 "Chemical analysis of water & waste", EPA Method 180 1 1978, EPA Washington DC.
12. EPA Office of Drinking Water. "Certification of laboratories analysing drinking water". Manual EPA Washington DC, 1992.
13. Standard Methods for the Examination of Water and Wastewater, 1995. Method 2130B

Biographical Notes:

John J Barron is Managing and Technical Director of Reagecon Diagnostics Limited. The company, which was founded in 1986, is the largest producer worldwide of Conductivity Standards and is also a major producer of other chemical standards. Mr. Barron is an expert in several areas of analytical chemistry, including electrochemical analysis, good laboratory practice (GLP) and chemical metrology. He has written and lectured extensively and is credited with several scientific discoveries including stable low level conductivity standards.

This paper forms part of a comprehensive series of papers that the authors have written covering all of the practical requirements for accurate analytical measurement. These papers are available via Reagecon's website at www.reagecon.com.